JOURNAL OF MATERIALS SCIENCE **37** (2002) 2781–2793

Surface characterization of electron beam modified dual phase filler by ESCA, FT-IR and surface energy

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Electron beam modification of carbon black (N220) and carbon-silica dual phase filler has been carried out at room temperature. The increase in oxygen to carbon ratio (O/C) determined by using Electron spectroscopy for chemical analysis (ESCA) is observed. Fourier transform infra-red spectroscopy (FT-IR) studies detect a new peak at 801 cm^{-1} upon electron beam irradiation, which is due to Si-C stretching in the case of modified dual phase fillers. The absence of the peak at 3400 cm^{-1} and the presence of the peak at 1720 cm^{-1} due to aliphatic ester stretching confirm the presence of trimethylol propane triacrylate (TMPTA) on the surface. Similarly, the absence of peak band at 3400 cm^{-1} confirms chemical interaction of triethoxysilylpropyl tetrasulphide (Si-69). A decrease in dispersive component (γ_s^d) and an increase in polar component (γ_s^p) of the surface energy corroborate surface oxidation. © *2002 Kluwer Academic Publishers*

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1. Introduction

The reinforcing effect of carbon black has the greatest influence on the usage of carbon black in the tire industry [1]. Today, carbon black plays an important role, not only as a reinforcing filler for tires, but also as a pigment for printing inks, coatings and plastics. Similarly, silica is used in a large number of rubber compounds. Both silica and carbon filled compounds have certain merits and demerits.

Recently, carbon-silica dual phase filler commercialized as "ECOBLACK" by Cabot corporation, has been designed to improve temperature dependence of hysteresis of filled rubber, by imparting improved traction and lower rolling resistance without sacrifice in wear resistance relative to conventional carbon blacks [2]. The dual phase fillers have high polymer-filler interaction than conventional carbon of comparable surface area [3].

Modification of carbon black filler by various techniques has been reported in the literature [4, 5]. Chemical oxidation of carbon black with nitric acid increases its ability to accept free radicals [6]. Treatment of high abrasion furnace carbon black (52 phr) surface with coupling agent such as aromatic titanates increases the tensile strength, elongation at break and tear resistance when loaded in styrene butadiene rubber (SBR) [7]. Recently, enhanced properties of electron beam modified filled fluorocarbon elastomer have been discussed [8]. It was conjectured that fillers and fluorocarbon rubber generate free radicals during electron beam treatment, which help in interaction between the components. But there is no report regarding electron beam modification of filler.

Dual phase fillers exhibit high polymer-filler interaction in the case of non-polar rubbers such as natural rubber (NR) and SBR due to its higher value of γ_s^d (dispersive component of surface energy) [9]. However, their utility for polar rubbers has not been understood. It is understood that by modification of a filler the property spectrum of the filler can generally be widened. It is with this objective in mind the present investigation has been undertaken. Also, quick modification of a filler at room temperature is an emerging technology. Carbon-silica dual phase filler has been modified by electron beam in absence and presence of monomer/silane coupling agent. The modified fillers

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have been characterized with the help of electron spectroscopy for chemical analysis (ESCA) and FT-IR spectra to understand the chemical changes upon electron beam irradiation. Further, surface energy of the modified fillers has been determined by dynamic wicking method. For comparison, fine particle carbon black (N220) and silica have been used.

2. Experimental

2.1. Materials

2.1.1. Fillers

Dual phase filler, carbon black and precipitated silica were supplied by Cabot Corporation, Billerica, USA, Philips Carbon Black Company, India and Bayer A. G. Germany respectively. The characteristics of the control fillers are given in Table I.

2.1.2. Chemicals

Trimethylol propane triacrylate (TMPTA) was supplied by UCB Chemicals, Belgium. Triethoxysilylpropyltetrasulphide (Si-69) was purchased from Degussa A. G., Germany. Potassium bromide of chemically pure grade (99%) was procured from Merck (India) Limited. Double distilled water and analytical grade formamide were used for the surface energy measurements.

2.2. Filler modification

TMPTA solution was prepared at a concentration of 3% in acetone in a beaker. This solution (100 c.c.) was poured into the filler sample (100 g) with stirring to completely wet the surface of filler. The mixture was then stirred thoroughly for 20 min at room temperature. The samples were then dried in air for 30 min. The samples (50 g) were then packed in polyethylene bags of size 0.18 × 0.2 m^2. The same procedure was followed for modification of the fillers by triethoxy silylpropyl tetrasulphide (Si-69).

2.3. Irradiation of samples

The packed samples were subjected to electron beam irradiation by using electron beam accelerator (Model ILU-6) at Bhabha Atomic Research Centre (BARC) Mumbai, India. The radiation dose was corrected for the dose absorbed by the polyethylene bag and the samples were subjected to a radiation dose of 10 Mrad (100 kGray). The specifications of the electron beam accelerator and operating principles of this accelerator can be seen elsewhere [10, 11].

TABLE I Analytical properties of dual phase fillers, carbon black and precipitated silica

Sample	Silicon (%) (ash analysis)	BET nitrogen surface area (m^2/g)	External surface area (STSA) (m^2/g)	CDBP (ml/100g)
CSDPF-A (CRX-2000)	4.8	167.0	121.4	101
CSDPF-E (CRX-2006)	5.7	210.8	136.7	104
N220	–	122	120	101
Precipitated silica	–	175	–	–

2.3.1. Designation of filler samples

Filler samples were designated as $A_{x/y}$, $B_{x/y}$, $C_{x/y}$ and $D_{x/y}$, where A represents the carbon black (N220), B and C represent the dual phase fillers and D represents the silica filler. x indicates the monomer or silane-coupling agent, while y represents the radiation dose in Mrad.

The filler designations are tabulated in the Table II.

TABLE II Designation of electron beam modified fillers

Sl. no.	Filler designation	Type of filler	Type of ingredient	Concentration of ingredient (%)	Radiation dose (kGray)
1	$A_{0/0}$	N220	–	–	–
2	$A_{0/10}$	N220	–	–	100
3	$B_{0/0}$	CSDPF-A	–	–	–
4	$B_{0/10}$	CSDPF-A	–	–	100
5	$B_{3T/10}$	CSDPF-A	TMPTA	3	100
6	$B_{3S/10}$	CSDPF-A	Si-69	3	100
7	$C_{0/0}$	CSDPF-E	–	–	–
8	$C_{0/10}$	CSDPF-E	–	–	100
9	$D_{0/0}$	Precipitated silica	–	–	–
10	$D_{0/10}$	Precipitated silica	–	–	100

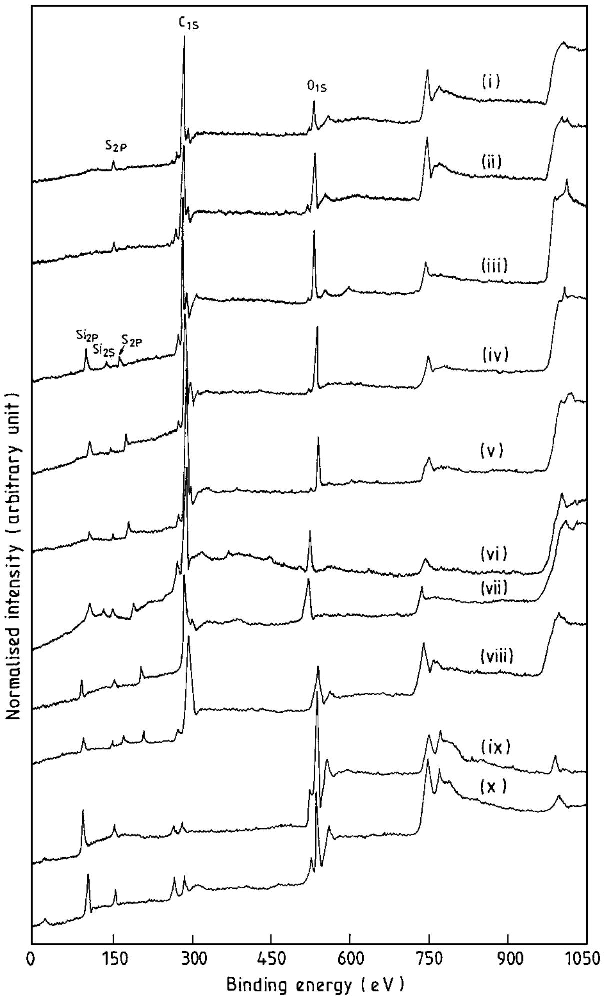


Figure 1 Survey scans of electron beam unmodified/modified fillers (i) $A_{0/0}$ (ii) $A_{0/10}$ (iii) $B_{0/0}$ (iv) $B_{0/10}$ (v) $B_{3T/10}$ (vi) $B_{3S/10}$ (vii) $C_{0/0}$ (viii) $C_{0/10}$ (ix) $D_{0/0}$ (x) $D_{0/10}$.

2.4. Characterization of electron beam modified carbon black, dual phase filler and silica

The chemical composition and the surface chemistry of electron beam modified carbon black (N220), Dual phase filler and silica were determined by the following techniques.

2.4.1. Electron spectroscopy for chemical analysis (ESCA)

ESCA data were obtained from VG Scientific ESCA Spectrometer, employing an exciting radiation of 1253.6 eV (Mg K_α) operating at 20 kV. The powder samples were pelletized and mounted with a double-sided adhesive tape onto the probe tip. The working pressure in the spectrometer was 4.3×10^{-9} torr and the electron take-off angle was 90°. The area under C1s, O1s and Si2p peaks were divided by the photoionisation cross-sectional area to calculate the concentration of each element present in the sample [12].

2.4.2. Infrared spectroscopy

Infrared spectra of the carbon black, dual phase fillers and silica samples were taken in the range of 4000 to 400 cm^{-1} with the help of "Nicolet Nexus Fourier Infra-Red Spectrophotometer" operating in Drift mode using Gemini Drift accessories. About 50 mg of carbon black was mixed with 500 mg KBr. 4 mg of the mixture was then mixed with 400 mg of KBr. The powder was then kept in the sample holder and FT-IR spectra were taken with an average of 100 scans at the resolution of 4 cm^{-1}. The same procedure was adopted for dual phase filler. For silica samples, about 50 mg of silica were mixed with 500 mg of KBr and 40 mg of the mixture was then mixed with 400 mg of KBr and FT-IR spectra were taken by adopting the same procedure as above. The concentrations of the fillers in KBr, as written above, were the optimized ones after the initial trial to get the best spectra.

2.4.3. Surface energy measurements using wicking method

The surface energy of the electron beam unmodified/modified dual phase fillers was calculated by the measurement of contact angle using a dynamic wicking method. The carbon black powder of 0.1 g was tapped 200 times and packed in the graduated capillary tube (2 mm inner diameter, 50 mm long). The tube was placed vertically and was contacted with liquid (water and formamide) in the beaker. The liquids penetrated up into the column of the powders by the capillary attraction. The height of the penetration was calculated by taking the weight of the penetrating liquid at regular intervals of time. The height of the liquid penetration was calculated using the relation [13].

$$h = \frac{w}{\rho S \in} \qquad (1)$$

where h = height of liquid penetration, ρ = density of filler sample, S = surface area of the powder in the packed column and $\in$ = porosity of the packed column.

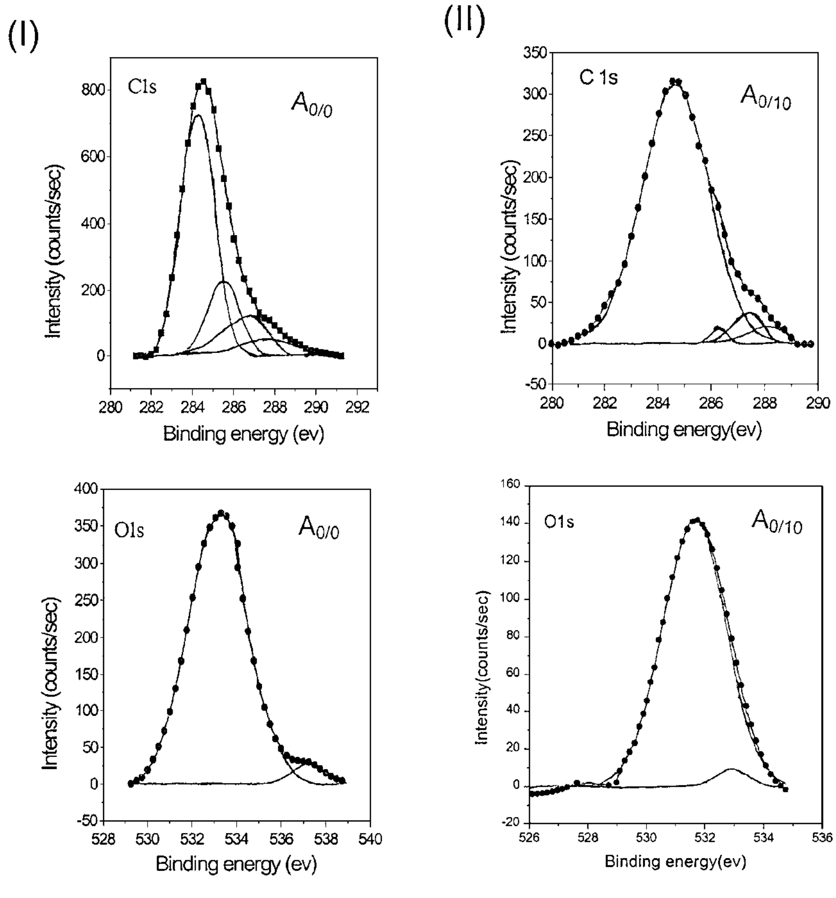


Figure 2 (I) Deconvoluted spectra of control carbon black ($A_{0/0}$). (II) Deconvoluted spectra of electron beam modified carbon black ($A_{0/10}$).

The contact angle of the powder samples with liquid was calculated using the Washburn equation [14].

$$h^2 = \frac{2 \cdot R_{\text{eff}} \cdot \gamma_{\text{L}} \cdot \cos\theta \cdot t}{\eta} \tag{2}$$

where $\gamma_{\text{L}} =$ surface tension of the liquid used, $\theta =$ contact angle of the liquid in the carbon black powder, $t =$ equilibrium time, $\eta =$ viscosity of the liquid, and $R_{\text{eff}} =$ effective radius of the packed column in the capillary tube.

The effective pore radius of the packed column was determined using Equation 2 and toluene as the spreading liquid. The surface energy of the dual phase filler was calculated by measuring the contact angle with water and formamide using the following equation [15].

$$\cos\theta = -1 + \frac{2\left(\gamma_{\text{s}}^{\text{d}} \cdot \gamma_{\text{l}}^{\text{d}}\right)^{1/2}}{\gamma_{\text{L}}} + \frac{2\left(\gamma_{\text{s}}^{\text{p}} \cdot \gamma_{\text{l}}^{\text{p}}\right)^{1/2}}{\gamma_{\text{L}}} \tag{3}$$

where $\gamma_{\text{s}}^{\text{d}} =$ dispersive component of the free energy of the solid surface, $\gamma_{\text{l}}^{\text{d}} =$ dispersive component of the free energy of the liquid surface, $\gamma_{\text{s}}^{\text{p}} =$ polar component of the free energy of the solid surface, $\gamma_{\text{l}}^{\text{p}} =$ polar component of the free energy of the liquid surface and $\gamma_{\text{L}} =$ surface tension of the liquid.

The values of $\gamma_{\text{l}}^{\text{d}}$ and $\gamma_{\text{l}}^{\text{p}}$ for water and formamide were taken from the literature [16].

3. Results and discussion

3.1. Electron spectroscopy for chemical analysis (ESCA)

3.1.1. Survey scans

Fig. 1 shows the survey scans of electron beam modified dual phase filler, carbon black and silica samples. The peaks at 284.5 and 530 are due to C1s and O1s binding energies respectively confirming the presence of carbon and oxygen in the carbon black filler. The peak at 100 eV, which is due to Si2p binding energy and the peak at 149 eV, which is Si2s binding energy, confirm the presence of silicon in the dual phase fillers. Upon electron beam irradiation, the intensity of the oxygen peak at 530 eV with respect to the carbon peak, C1s, at 284.5 eV increases, indicating oxidation of the carbon black and the dual phase fillers. In the case of monomer modified dual phase filler, the increase in intensity peak value at 284.5 eV confirms the presence of the monomer. An increase in sulphur peak intensity at 229 eV confirms the presence of Si-69 in the dual phase filler modified with silane coupling agent (Si-69). In the case of precipitated silica, the peaks at 530 and 100 eV show the presence of oxygen and silicon. Also, a small peak at 284.5 eV confirms the presence of carbon in the precipitated silica.

3.1.2. Carbon (1s) spectra

The carbon (1s) peak binding energy and peak widths are tabulated in Table III and the spectra are given in Figs 2–6. The carbon peak binding energies for all the samples are located around 284.5 eV. The full width at half of the height maximum (FWHM) increases for all carbon blacks, subjected to electron beam irradiation indicating surface oxidation. In the case of dual phase filler treated with 3% TMPTA ($B_{3T/10}$) FWHM shows an increase (1.58 eV) compared to the control (1.39 eV), indicating the presence of new species on the surface. Also, a decrease in peak position from 284.6 eV to 284.3 eV confirms the presence of the TMPTA on the surface of the filler. The increase in FWHM value from 1.39 eV ($B_{0/0}$) to 1.59 eV ($B_{0/10}$) confirms the surface oxidation of dual phase filler on simple irradiation. The same trend is found in the case of the dual phase filler modified with silane coupling agent followed by electron beam irradiation. The carbon peak in the case of precipitated silica indicates incorporation of carbon during manufacturing. An increase in FWHM value (3.03 eV) of silica sample subjected to electron beam irradiation with radiation dose of 10 Mrad (100 kGray) confirms the oxidation of carbon in the silica sample.

Deconvolution of carbon peak reveals the presence of C—O groups (around 286.0 eV), C=0 groups (around 287.5 eV), —COO— groups (around 288.8 eV) and a satellite peak at around 290.2 eV due to the π–π^* transition in double bond of the aromatic group in the carbon black and dual phase fillers [17, 18].

3.1.3. Silicon (Si 2p) spectra

Silicon (2p) spectra of electron beam modified carbon black, dual phase and silica fillers are also shown

TABLE III ESCA peak binding energy and peak width at half of maximum height

Sl. no.	Filler designation	Carbon		Silicon		Oxygen	
		Position (eV)	FWHM (eV)	Position (eV)	FWHM (eV)	Position (eV)	FWHM (eV)
1	$A_{0/0}$	284.6	1.46	NP	NP	532.1	1.70
2	$A_{0/10}$	284.5	1.86	NP	NP	531.7	2.05
3	$B_{0/0}$	284.6	1.39	103.6	2.20	533.0	1.60
4	$B_{0/10}$	284.5	1.59	102.9	2.30	532.0	1.94
5	$B_{3T/10}$	284.3	1.58	103.0	2.15	532.7	2.30
6	$B_{3S/10}$	284.3	1.61	101.5	2.68	532.4	1.97
7	$C_{0/0}$	284.6	1.59	103.0	2.01	532.4	1.60
8	$C_{0/10}$	284.5	1.76	102.5	2.50	532.1	1.65
9	$D_{0/0}$	284.5	2.90	102.9	2.59	532.4	2.10
10	$D_{0/10}$	284.5	3.03	102.8	2.59	532.0	2.30

NP: No peak.

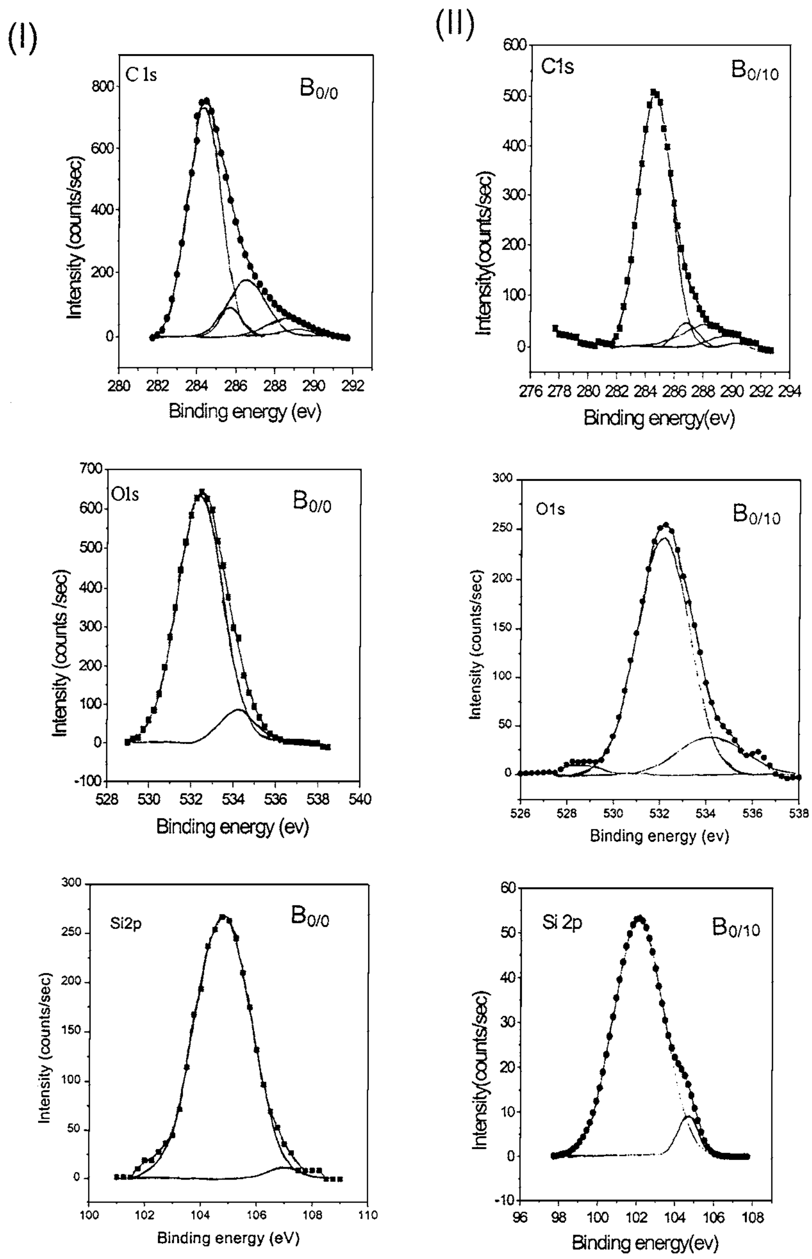


Figure 3 (I) Deconvoluted spectra of control dual phase filler ($B_{0/0}$). (II) Deconvoluted spectra of electron beam modified dual phase filler ($B_{0/10}$).

in Figs 2–6 and the peak positions are tabulated in Table III. The increase in FWHM value of silica from 2.2 eV ($B_{0/0}$) to 2.3 eV ($B_{0/10}$) indicates the changes on the surface of silica upon electron beam irradiation. Also, decrease in the peak value from 103.6 eV to 102.9 eV confirms the same. In the case of dual phase filler modified with silane coupling agent ($B_{3S/10}$), an increase in FWHM value from 2.20 eV ($B_{0/0}$) to 2.68 eV ($B_{3S/10}$) with a corresponding decrease in the peak position from 103.6 eV ($B_{0/0}$) to 102.9 eV ($B_{0/10}$) confirms the fact that Si-69 reacted with surface silanol groups. In the case of monomer modified dual phase filler ($B_{3T/10}$), the two peaks at 103 eV and 104.5 eV are formed due to Si—OH and Si—O—Si bonds.

3.1.4. Oxygen (1s) spectra

Oxygen (1s) spectra of the electron beam modified carbon black filler, dual phase filler and pure silica are shown in Figs 2–6. The FWHM values (Table III) of oxygen show that electron beam irradiation in the presence of air results in surface oxidation. In the case of TMPTA modified dual phase filler ($B_{3T/10}$), the FWHM value increases from 1.60 eV ($B_{0/0}$) to 2.30 eV ($B_{3T/10}$), which confirms the presence of acrylate group on the surface. The increase in FWHM value from 2.10 eV($D_{0/0}$) to 2.30 eV ($D_{0/10}$) confirms the surface oxidation in silica samples.

Upon deconvolution, three peaks are observed. The peak maximum occurs at around 532.8 eV which is due to C—OH groups on the surface. For the electron beam irradiated fillers ($A_{0/10}$, $B_{0/10}$, $C_{0/10}$) the peak maximum shifts to 532 eV which reveals that more C=O groups (peak position of C=O group 531.8 eV) are introduced on the surface. In the case of dual phase filler modified with Si-69 ($B_{3S/10}$), the peak maximum occurs at 532.2 eV which is due to C—O—C binding energy (peak position 532.4 eV). This confirms the reaction between Si-69 and C—OH groups.

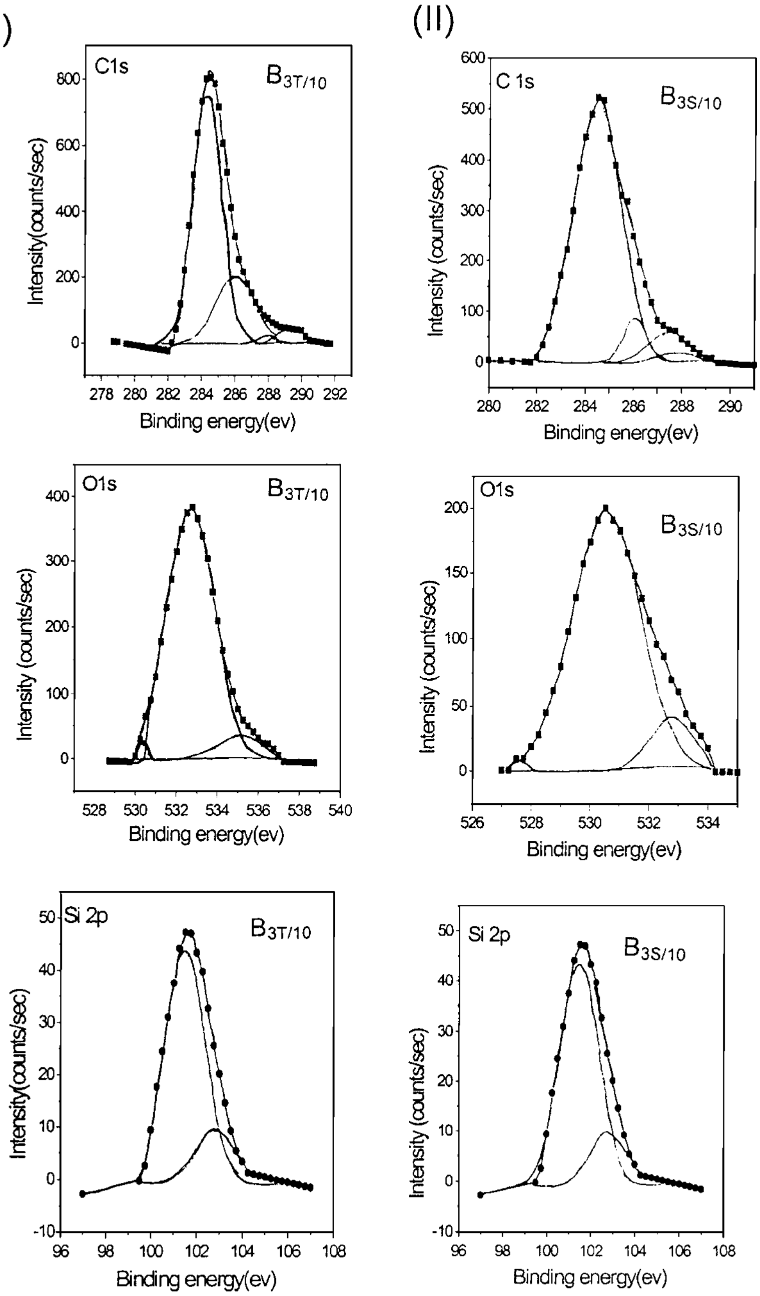


Figure 4 (I) Deconvoluted spectra of electron beam modified dual phase filler ($B_{3T/10}$). (II) Deconvoluted spectra of electron beam modified dual phase filler ($B_{3S/10}$).

3.1.5. Quantitative estimation

Quantitative estimation can be done by measuring the area under the peak. Atomic percentage is calculated using the relation [19]:

$$C_j = \frac{A_i S_i}{\sum_j^m A_j S_j} \tag{5}$$

where A_i = Area under the peak of element "i", S_i = Sensitivity factor of element "i", m = No. of elements in the sample and i and j represent the elements.

Atomic percentages of carbon, silicon, oxygen and sulphur are tabulated in Table IV. Carbon percentage on the surface decreases from 87.50% to 83.20% and oxygen percentage increases from 9.0 to 13.2% in the case of dual phase filler $B_{0/0}$ (CSDPF-A) upon electron beam irradiation with radiation dose of 10 Mrad (100 kGray). O/C ratio increases from 0.10 to 0.16 in the case of dual phase filler CSDPF-A ($B_{0/0}$). However there is no noticeable change in Si/C ratio. In the case of $B_{3T/10}$, Si/C ratio decreases from 0.04 ($B_{0/0}$), to

TABLE IV Quantitative atomic percentages by ESCA

Sl. no.	Filler designation	Carbon (%)	Silicon (%)	Oxygen (%)	Sulphur (%)	O/C ratio	O/Si ratio	Si/C ratio
1	$A_{0/0}$	93.20	0.00	6.80	0.20	0.07	–	–
2	$A_{0/10}$	88.60	0.00	11.15	0.11	0.13	–	–
3	$B_{0/0}$	87.50	3.30	9.00	0.20	0.10	0.04	2.73
4	$B_{0/10}$	83.20	3.50	13.20	0.15	0.16	0.04	3.77
5	$B_{3T/10}$	86.50	2.60	10.80	0.20	0.13	0.03	4.15
6	$B_{3S/10}$	85.13	4.70	10.00	0.27	0.12	0.06	2.10
7	$C_{0/0}$	86.50	4.30	9.00	0.20	0.10	0.05	2.09
8	$C_{0/10}$	82.88	4.54	12.38	0.20	0.15	0.06	2.73
9	$D_{0/0}$	6.20	38.00	55.60	0.00	8.97	6.20	1.46
10	$D_{0/10}$	18.70	26.84	49.90	0.00	2.67	1.44	1.86

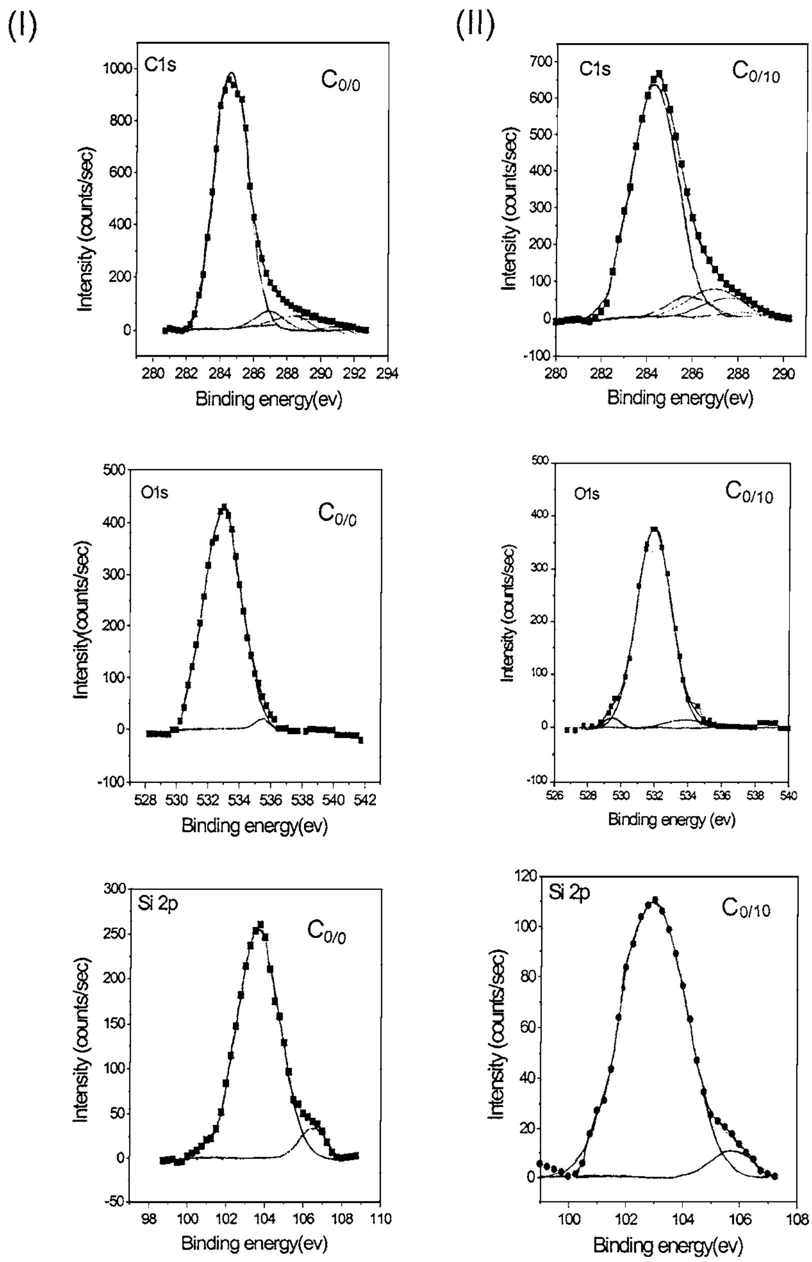


Figure 5 (I) Deconvoluted spectra of control dual phase filler ($C_{0/0}$). (II) Deconvoluted spectra of electron beam modified dual phase filler ($C_{0/10}$).

0.03 ($B_{3T/10}$), which is due to the presence of TMPTA monomer on the surface. In the case of pure silica, some interesting results are obtained. Upon electron beam irradiation, carbon in the case of precipitated silica gets oxidized, but at the same time surface silanol groups are dehydrated to siloxane rings, which predominate over carbon oxidation resulting in the decrease of oxygen concentration on the surface of silica. As a consequence there is an increase in relative atomic percentage of carbon.

3.1.6. Diffuse reflectance infra-red Fourier transform spectral studies

Infrared spectroscopy is an extremely powerful analytical technique for both qualitative and quantitative analysis. Diffuse reflectance infrared spectral studies give distinct peaks of stretching and bending vibrations of various functional groups. Carbon black is a complex structure containing a lot of functional groups on the surface such as lactones, quinones, and phenol that are having characteristic absorption bands. Fig. 7a shows the complete spectra of carbon black, dual phase filler and silica in the range of 4000 to 400 cm^{-1}. The characteristic absorption band due to stretching and bending vibrations of carbon black, dual phase filler and silica are tabulated in Table V. The peak above 3000 cm^{-1} can give the information about the Si—OH and C—OH groups, but this is totally hidden by the large water band 3400 cm^{-1} in the case of carbon black, dual phase filler and silica. The peaks at 2922 cm^{-1} and 2855 cm^{-1} corresponds to —CH assymetric stretching and —CH_2 stretching of various lactone rings. The peak around 1700 cm^{-1} is due to >C=O stretching vibration of lactones and the peak at 910 cm^{-1} corresponds to C—C skeletal vibration in carbon black and dual phase fillers. Also, the peak at 680 cm^{-1} corresponds to C—S stretching vibration in carbon black and dual phase fillers. The expanded spectra of carbon black, dual phase filler and silica in the range of 3000 to 1300 cm^{-1} and 1250 to 750 cm^{-1} are displayed in Fig. 7b and c.

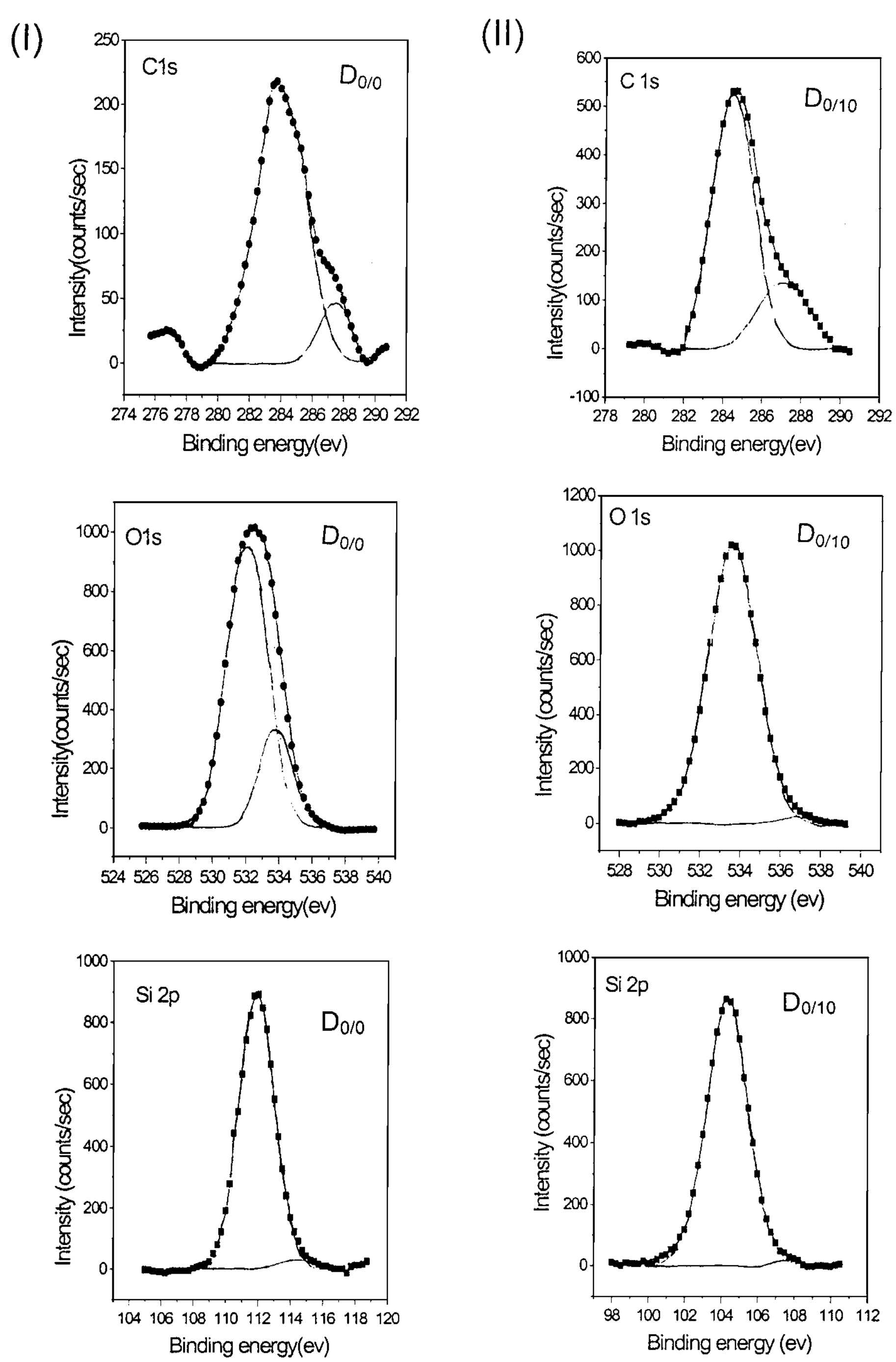


Figure 6 (I) Deconvoluted spectra of control silica sample ($D_{0/0}$). (II) Deconvoluted spectra of electron beam modified silica ($D_{0/10}$).

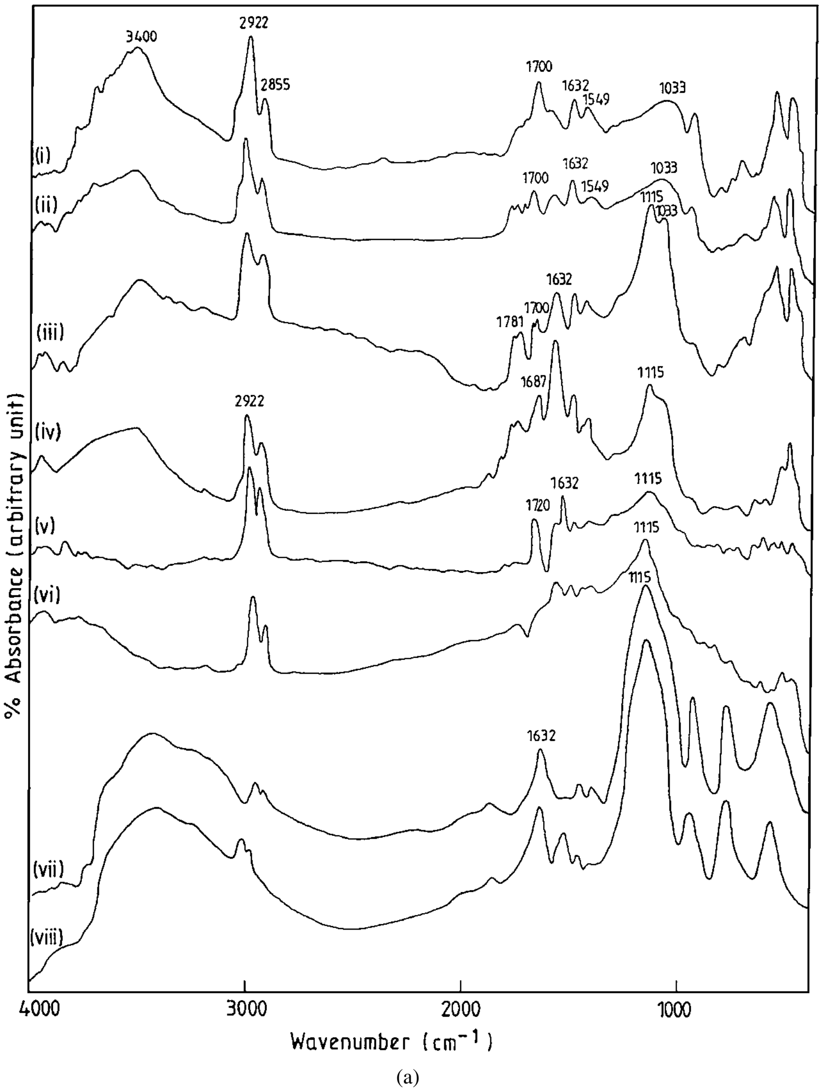
Several peaks are found at around 1700 cm^{-1} that confirm the presence of different lactone rings in the case of carbon black fillers ($A_{0/0}$). The peak at 1632 cm^{-1} is due to >C=C< stretching vibration of unsaturated groups in lactone rings which decreases upon irradiation due to oxidation. The peaks at around 1549 cm^{-1}, broadened upon irradiation may be attributed to the formation of cyclic structures upon irradiation.

In the case of dual phase filler ($B_{0/0}$) the peak at 1782 cm^{-1} corresponds to the α,β-unsaturated γ-lactone rings, and the peak at 1740 cm^{-1}, corresponds to δ-lactone rings [20]. An increase in intensity of these peaks upon irradiation confirms the surface oxidation is the case of electron beam modified dual phase filler ($B_{0/10}$). The peak at 1687 cm^{-1} may be due to the hydrogen bonded >C=O on the surface of dual phase fillers. The increase in intensity at 1549 cm^{-1} may be due to the formation of cyclic structures on the surface. The peak at 1389 cm^{-1} shows interaction of unsaturated groups and silica networks resulting in Si—CH=CH_2 groups upon irradiation ($B_{0/10}$). The small peak at 801 cm^{-1}, which is due to SiC vibration confirms the above fact. An increase in peak height at 1115 cm^{-1} due to Si—O stretching vibration and decrease in peak intensity at 1033 cm^{-1} which corresponds to C—O—C group upon irradiation confirm the oxidation. The peak at 915 cm^{-1}, which corresponds to Si—O stretching of Si—OH groups decreases upon irradation and confirms the dehydration of silanol groups.

In the case of monomer modified dual phase filler, absence of broad peak at 3400 cm^{-1} confirms the absence of —OH group on the surface. Also increase in peak height at 2922 cm^{-1} and 2855 cm^{-1} and the peak at 1621 cm^{-1} confirm the presence of TMPTA on the surface. The absence of peaks at 1781 and 1740 cm^{-1} in the case of TMPTA modified dual phase filler ($B_{3T/10}$) may be attributed to the surface coating of TMPTA on the dual phase filler. The broad peak at 1720 cm^{-1} which corresponds to the >C=O stretching frequency of acrylate group and the peak at 840 cm^{-1} confirm the presence of acrylate group. The peak at 1389 cm^{-1} indicates interaction of unsaturated groups in TMPTA and silica networks resulting in Si—CH=CH$_2$ groups upon irradiation ($B_{3T/10}$). This is confirmed from the Si—C stretching vibration of TMPTA modified dual phase filler. The absence of peak at 915 cm^{-1} which is due to Si—O stretching of Si—OH group confirms the chemical interaction of TMPTA with silanol groups.

The absence of broad peak at 3400 cm^{-1} shows the absence of OH group on the surface which proves the chemical interaction of dual phase filler with silane coupling agent. The broad peak at 1115 cm^{-1} which is due to Si—O—Si and Si—O—C groups also confirms the presence of Si-69 on the surface of dual phase fillers. New peak at 955 cm^{-1} due to Si—O—CH$_2$ symmetric deformation and two peaks at 915 cm^{-1} corresponding to the Si—O—Ar stretching confirm the reaction between phenolic-OH group and Si-69. The peak at 1440 cm^{-1} corresponding to the ring vibration of Si-Ph and a broad peak at 802 cm^{-1} corroborate the chemical interaction of silica networks with carbon phase upon irradiation.

In the case of silica, the broad peak at 3400 cm^{-1} is due to water band. The peak at 1630 cm^{-1} corresponds to the water adsorbed silica. The peak at 1115 cm^{-1}, corresponds to the Si—O stretching of silica and the peak at 485 cm^{-1} is due to disiloxane ring vibration. The peak at 960 cm^{-1} corresponds to Si—O stretching vibration of Si—OH group. Upon irradiation an increase of peak height of Si—O—Si peak and a decrease of peak height of Si—OH confirm the dehydration reaction in silica groups.



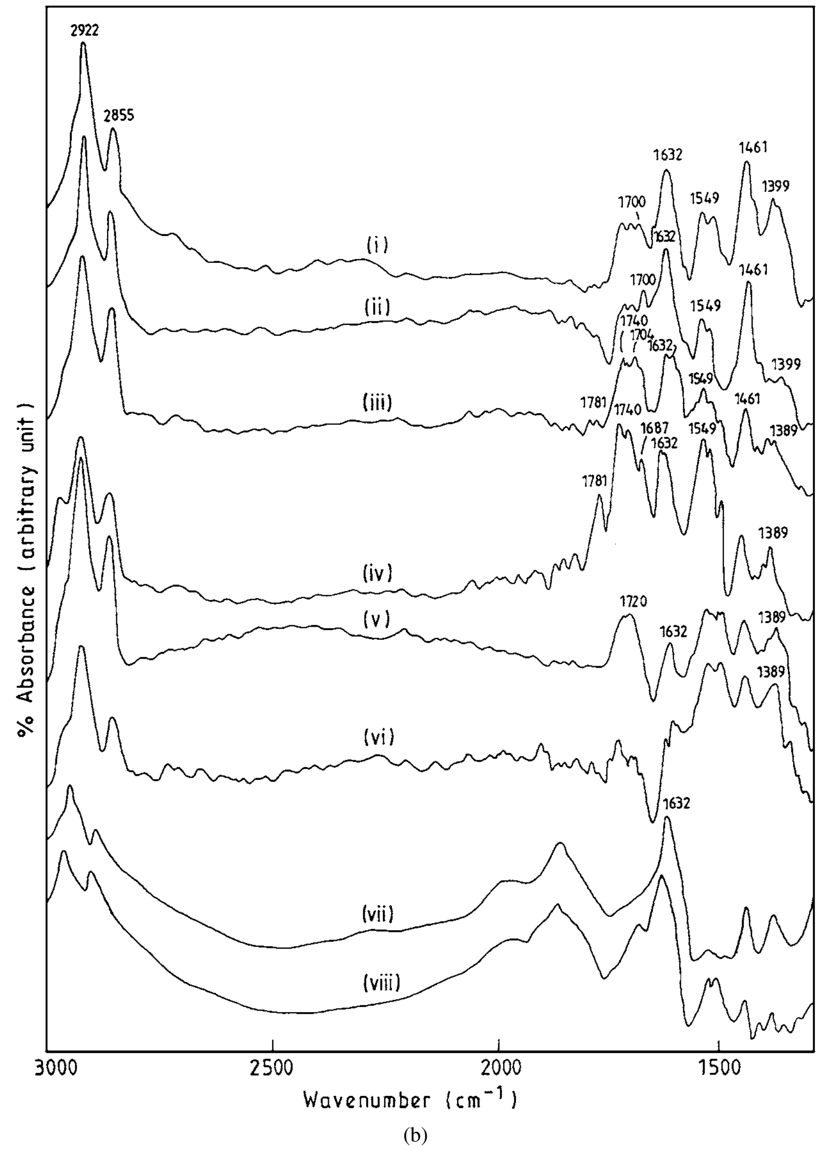
(a)

Figure 7 (a) FT-IR spectra's of electron beam modified carbon black, dual phase fillers and silica fillers is the region of 4000–400 cm^{-1} (i) $A_{0/0}$ (ii) $A_{0/10}$ (iii) $B_{0/0}$ (iv) $B_{0/10}$ (v) $B_{3T/10}$ (vi) $B_{3S/10}$ (vii) $D_{0/0}$ (viii) $D_{0/10}$. (b) Expanded FT-IR spectra's of electron beam modified carbon black, dual phase fillers and silica fillers in the regtion of 3000–1300 cm^{-1} (i) $A_{0/0}$ (ii) $A_{0/10}$ (iii) $B_{0/0}$ (iv) $B_{0/10}$ (v) $B_{3T/10}$ (vi) $B_{3S/10}$ (vii) $D_{0/0}$ (viii) $D_{0/10}$. (c) Expanded FT-IR spectra's of electron beam modified carbon black, dual phase fillers and silica fillers in the region of 1250–750 cm^{-1} (i) $A_{0/0}$ (ii) $A_{0/10}$ (iii) $B_{0/0}$ (iv) $B_{0/10}$ (v) $B_{3T/10}$ (vi) $B_{3S/10}$ (vii) $D_{0/0}$ (viii) $D_{0/10}$. (*Continued.*)

3.1.7. Surface energy measurements by wicking method

Wicking is the measurement of the contact angle, which liquids make with the particulate solids, by determining the rate of capillary rise of these liquids in packed beds of such materials. Surface energy measurement has been done for the B samples. Fig. 8 a and b shows wicking results with two liquids—water and formamide. In general, the weight of the liquids increases rapidly with time in the initial stage. There is a limiting value for water within a few minutes of the experiments and the amount of water uptake is quite high. Penetration of formamide in the capillary continues to increase even after 35 min. The weight of the penetrating water in dual phase filler subjected to a radiation dose of 100 kGray increases upon electron beam irradiation compared to the dual phase filler modified with TMPTA and silane coupling agent (Si-69). The same increasing trend with time is observed in the case of wicking with formamide. The surface energy is determined using the Fowkes equation.

The surface energy results are tabulated in Table VI. Upon electron beam irradiation, γ_s^d is found to decrease, whereas γ_s^p increases. The oxygen atoms screen some original energetic spots, which results in the lowering of γ_s^d value of electron beam modified dual phase fillers. In the case of dual phase filler modified with TMPTA, γ_s^d increases, which may be due to the formation of high energy sites on the surface having greater unsaturated $-COO-CH=CH_2$ group [21]. γ_s^p value is highest for $B_{0/10}$ samples, although the value of γ_s^p $B_{3T/10}$ and $B_{3S/10}$ are higher than that of $B_{0/10}$. These results are in accordance with the ESCA & FTIR results, suggesting that γ_s^p values are controlled by the polarity of the surface. The surface energy, γ, is found to be highest for $B_{3T/10}$ sample, due to a very high value of γ_s^d. In the case of carbon black surface modified with silane coupling agent ($B_{3S/10}$), γ_s^d is found to be high compared to control sample ($B_{0/0}$), but lower than that of $B_{3T/10}$. Treatment of dual phase filler with silane coupling agent (Si-69) reduces the filler-filler interaction due to hydrogen bonding, which results in more crystal edges which are active sites on the surface resulting in an increase of γ_s^d. The values reported in Table VI for dual phase filler are however low compared to the results in the earlier references

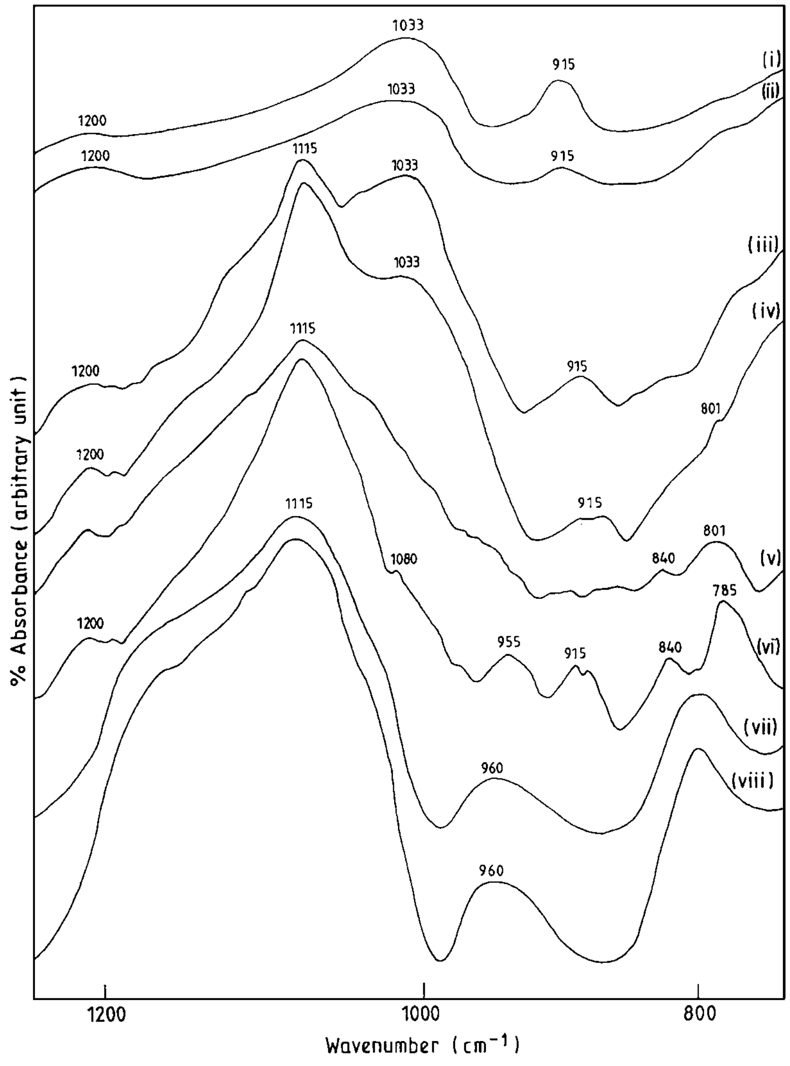


(b)

Figure 7 (*Continued*.)

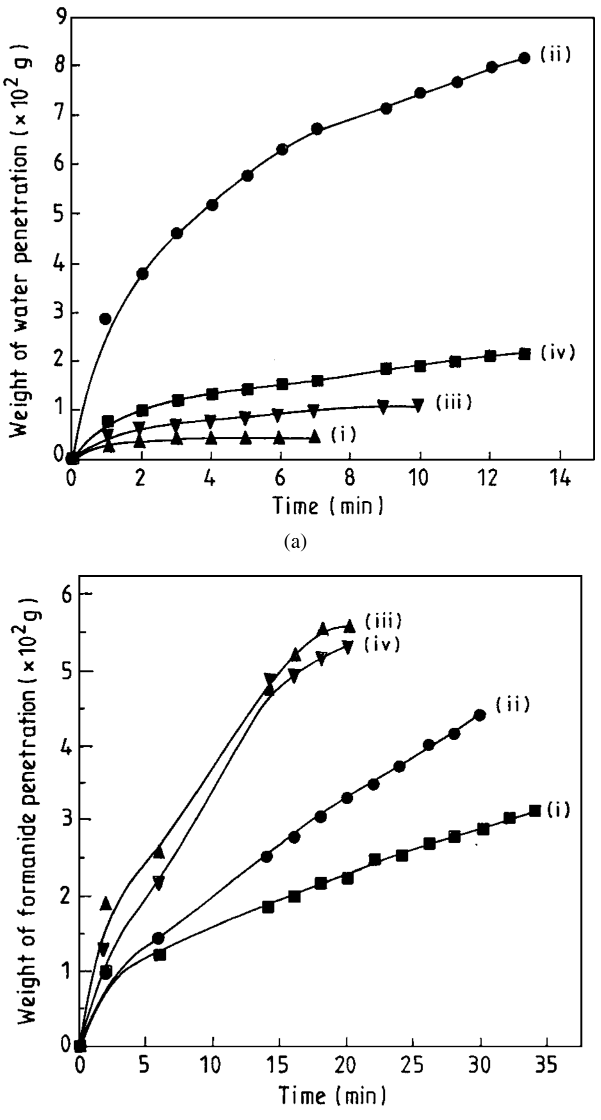
TABLE V Peak assignments of electron beam modified carbon black, dual phase filler and silica determined by FT-IR studies

Sl. no.	Wave number (cm^{-1})	Functional groups
	Common peaks for control/electron beam modified dual phase fillers, carbon black and silica	
1	3402	Broad spectra due to large water band on the surface of the carbon black, dual phase filler and silica
2	2922	–CH stretching frequency of lactones in carbon black & dual phase fillers
3	2855	–CH_2 stretching frequency of lactones in carbon black & dual phase fillers
4	1743 1734	$>C{=}O$ stretching frequency of δ-lactone ring in the carbon black and dual phase fillers (fermi resonance)
5	1720	$>C{=}O$ stretching frequency of quinones in carbon black, dual phase filler
6	1633	$>CH{=}CH<$ stretching vibration in α, β-unsaturated lactone ring
7	1549	$>CH{=}CH<$ stretching vibration of substituted benzenes
8	1461	$>CH$ bending frequency of hydrocarbon in carbon black & dual phase filler and silica
9	1115	Stretching vibration of SiO_2 networks (i.e.) Stretching vibration due to tetramer siloxane ring in dual phase fillers and silica
10	1033	C–O–C symmetric stretching in the case of dual phase fillers and carbon black
11	910	C–C skeletal vibration of cyclic rings
12	680	C–S stretching vibration in carbon black and dual phase fillers
13	530	Ring out of plane bendings of substituted benzenes
14	490	Symmetric disiloxane (Si–O–Si)
	Peaks in electron beam modified carbon black, dual phase fillers and silica	
15	1781	$>C{=}O$ stretching vibration of γ-lactones in the case of electron beam modified dual phase fillers ($B_{0/10}$)
16	1440	Ring vibration of Si–Ph
17	1389	CH_2 vibration of Si–CH=CH_2
18	801	Si–C stretching vibration



(c)

Figure 7 (*Continued*.)



(a)

(b)

Figure 8 (a) Penetration rate of water into the packed column of dual phase filler (i) $B_{0/0}$ (ii) $B_{0/10}$ (iii) $B_{3T/10}$ (iv) $B_{3S/10}$. (b) Penetration rate of formamide into the packed column of dual phase fillers (i) $B_{0/0}$ (ii) $B_{0/10}$ (iii) $B_{3T/10}$ (v) $B_{3s/10}$.

TABLE VI Surface energy (γ) and its components for electron beam modified dual phase filler determined by wicking experiment at 25°C

		Surface energy		
Sl. no.	Filler designation	Dispersive component ($\gamma_s{}^d$) mJ/m^2	Polar component ($\gamma_s{}^p$) mJ/m^2	Total surface energy (γ) mJ/m^2
1	$B_{0/0}$	71.3	0.6	71.9
2	$B_{0/10}$	66.0	7.2	73.2
3	$B_{3T/10}$	110.4	2.7	113.1
4	$B_{3S/10}$	94.2	1.6	95.8

due to temperature dependence of γ_s^d and a different method used [22]. In the later case, the author measured the surface energy at 180°C using inverse gas chromatography.

4. Conclusions

Electron beam modification of carbon black (N220), dual phase fillers and silica samples in presence of TMPTA and silane coupling agent (Si-69) was done and the samples were characterized by ESCA, FT-IR and surface energy measurements. Following conclusions were made:

(i) From ESCA results, the shift of peak maximum from 532.4 eV to 531.8 eV and increase in % of oxygen confirm the surface oxidation upon electron beam irradiation. An increase in carbon percentage of TMPTA modified dual phase filler ($B_{3T/10}$) and an increase in silicon percentage in silane modified dual phase filler ($B_{3S/10}$) reveal the presence of TMPTA and TESPT respectively on the surface of dual phase fillers.

(ii) FT-IR studies indicate a new peak at 801 cm^{-1}, which is due to Si-C stretching. The absence of peak band at 3400 cm^{-1} and the peak at 1720 cm^{-1} due to aliphatic ester stretching confirm the presence of TMPTA on the surface. The chemical interaction of triethoxysilylpropyltetrasulfide with dual phase filler is confirmed by the absence of peak band at 3400 cm^{-1} and an increase in peak intensity value at 1115 cm^{-1}, which is due to Si—O stretching vibration of Si—O—C group.

(iii) A decrease in γ_s^d value and an increase in γ_s^p also corroborate surface modification in the case of electron beam modified dual phase filler ($B_{0/10}$). The high γ_s^d value of TMPTA modified dual phase filler was due to the unsaturated sites on the surface.

Acknowledgement

The authors are grateful to Dr. M. J. Wang, Cabot Corporation, USA for providing the dual phase fillers.

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Received 19 April 2001
and accepted 14 February 2002